Japanese Kokai Patent Application No. Sho 60[1985]-239740

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KOKAI PATENT APPLICATION NO. SHO 60[1985]-239740

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RECORDING MEDIUM

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[There are no amendments to this patent.]

Claim

A recording medium in which a monomolecular film or a built-up monomolecular layer film comprising a host molecule having a hydrophilic group, a hydrophobic group, and an inclusion group, and a guest molecule included in the above-mentioned host molecule is produced on a carrier to form a recording layer, and recording is performed through application of light.

Detailed explanation of the invention

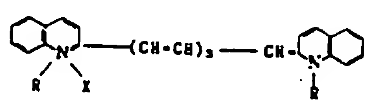
(1) Technical field

The present invention pertains to a recording medium in which recording is performed by utilizing the chemical or physical change in a monomolecular film consisting of an inclusion complex or built-up monomolecular layer film.

(2) Technical background

A variety of recording media having an organic compound for the recording layer have been known.

For example, an optical recording medium in which a thin film organic compound is used as the recording layer is disclosed in, Japanese Kokai Patent Application Nos. Sho 56[1981]-16948 and Sho 58[1983]-125246. In each case, the invention pertains to a laser recording medium in which an organic color material is used as the recording layer, and recording and playback are achieved with a laser beam. In particular, the medium disclosed in Japanese Kokai Patent Application No. Sho 58[1983]-125246 has a recording layer consisting of a thin film of a cyanine dye indicated by general formula (I) below


(I)

The cyanine dye indicated by general formula (I) is coated on a plastic base to a thickness of 1000 Å or less, for example, a thickness of approximately 300 Å, by means of a rotary coating

machine, and a thin film is produced. When the molecular orientation and distribution within the film is random, optical scattering occurs within the film when light irradiation is applied, and the degree of the chemical reaction that occurs upon application of each type of radiation varies on a microscopic level. For this reason, a recording medium with a uniform molecular distribution and orientation within the molecular layer is desirable, and a reduced film thickness is required for increased recording density. However, when a coating method is used, the limitation in thickness of the film is approximately 300 Å, and random molecular distribution and orientation within the film was difficult to control.

It is stated in Japanese Kokai Patent Application Nos. Sho 56[1981]-42229 and Sho 56[1981]-43220 that a built-up film comprised of a diacetylene compound with a significant photonic effect and an excellent high resolution suggested as a resist material can be applied to thin-film electrooptical devices, electroacoustic devices, piezoelectric devices, etc., as well as resist materials.

Recently, an improvement in the method for manufacturing diacetylene built-up films has been disclosed in Japanese Kokai Patent Application No. Sho 58[1983]-111029. The diacetylene built-up film produced on a base by the method described in the above-mentioned invention undergoes polymerization upon application of ultraviolet light and produces a diacetylene polymer film, or masking is used and ultraviolet light is applied to perform localized polymerization and the nonpolymerized portion is removed to produce a pattern, and the result is used as a thin-film optical device or integrated circuit element.

However, all of the above-mentioned methods are limited to diacetylene compounds, and the possibility of erasure of the recording when used as a thin-film optical device is not discussed at all.

Meanwhile, as a means to eliminate the above-mentioned problems, an optical recording medium that can be used repeatedly is produced by forming a recording layer consisting of a monomolecular film or built-up monomolecular layer film comprised of at least a photopolymeric monomer containing a hydrophilic group, a hydrophobic group, and having at least one unsaturated bond in the molecule on a base and is disclosed in Japanese Patent Application No. Sho 58[1983]-190932.

In all of the above-mentioned diacetylene built-up films and monomolecular films or built-up monomolecular layer films comprised of a photopolymeric monomer, a method for manufacturing in which hydrophilic and hydrophobic groups are introduced to the photo-sensitive compound, which is deposited directly on a base, is used. As a result, it is difficult to produce films with different functions using a simple method, and a reduction in the photo-sensitivity of the film results from induction of the hydrophilic groups and hydrophobic groups. Furthermore, to control the molecular orientation within the film, which is very important for high-density recording, a very complex operation is required.

In an effort to eliminate the above-mentioned problems with the conventional technology and as a result of their research on 1) a method for producing a variety of functional films using a relatively simple method, 2) a method in which the above-mentioned film formation is carried out such that the

functional properties of the molecule are not reduced even when a thin film is used, and 3) a method in which orientation of the molecules in the film is carried out in the in-plane direction of the film to provide high orientation without a special operation, and thereby, the present invention was accomplished. Furthermore, it was possible to easily produce a high-quality recording medium with high sensitivity and high resolution using the above-mentioned method.

(3) Disclosure of the invention

The objective of the present invention is to produce a high-density recording medium capable of a chemical or physical change in the molecule upon exposure to light.

Also, the objective is to produce a superior medium, compared to those produced by conventional methods, with regard to the molecular orientation within the plane of the medium, which is an important factor for high-density recording at the molecular level. Furthermore, the objective is to produce a medium with different properties produced through relatively simple changes in the operation during production of the above-mentioned recording medium.

The above-mentioned objectives of the present invention can be achieved by the present invention described below.

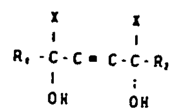
A recording medium in which a monomolecular film or a built-up monomolecular layer film comprised of a host molecule having a hydrophilic group, a hydrophobic group, and a group where inclusion (inclusion group) of other molecules is made possible (host molecule), and a different type of molecule

included by a host molecule (guest molecule) is produced on a carrier to form a recording layer, and recording is carried out through application of light.

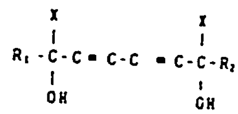
A material that comprises the recording layer of the present invention consists of two types of molecules, a molecule having at least one group containing a hydrophilic group, a hydrophobic group, and a group whereby inclusion of a different molecule is made possible (which is referred to as the host molecule), and a different type of molecule included in the above-mentioned host molecule (which is referred to as the guest molecule). When the monomolecular film, or built-up monomolecular layer film consisting of the inclusion complex comprised of the above-mentioned host molecule and guest molecule is deposited on a carrier, the recording medium of the present invention can be produced. Between the above-mentioned two types of molecules, it is necessary for one or both of them to change either chemically or physically as a result of exposure to light. In other words, in the recording medium of the present invention, recording is carried out utilizing the above-mentioned chemical or physical change.

The host molecules that can be used in the present invention, as described above, are molecules having a hydrophilic group, a hydrophobic group, and a group capable of forming at least one inclusion complex with a different type of molecule, and it is not especially limited. As typical examples of structural elements capable of forming the hydrophilic group or hydrophobic group within the molecule, a variety of commonly known hydrophilic groups and hydrophobic groups can be mentioned. The group capable of forming an inclusion complex with a

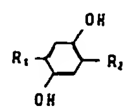
different type of molecule can be produced by introduction of hydroxy groups, carbonyl groups, carboxyl groups, ester groups, amino groups, nitrile groups, thioalcohol groups, imino groups, etc. In the following, the above-mentioned host molecule is explained in specific terms using a host molecule having hydroxy groups indicated by general formulas (IIa)-(IIc) as examples.



(IIa)



(IIb)



(IIc)

(In this case, X = H or C_6H_5.)

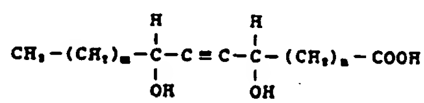
In other words, having a hydrophilic group and a hydrophobic group within the molecule means, for example, in the above-mentioned chemical formula, a hydrophilic group exists on either the R_1 group or the R_2 group, and a hydrophobic group exists on the other, or both the R_1 group and the R_2 group exhibit hydrophilic properties or hydrophobic properties in relation to the groups other than those two. Regarding the formula of the R_1 group and the R_2 group, when a hydrophobic group is to be introduced, a long-chain alkyl group with 5-30 carbon atoms is especially suitable, and when a hydrophilic group is to be

introduced, a fatty acid with 1-30 carbon atoms is especially suitable.

As a specific example of the host molecule used in the present invention, acetylene diol derivatives (Nos. 1-6, and Nos. 16-21), diacetylene diol derivatives (Nos. 7-12, and Nos. 22-27), hydroquinone derivatives (Nos. 13-15, and Nos. 28-30), etc., can be mentioned as suitable examples. It should be noted that, in the following, m and n each represent a positive number, and Z represents $-CH_3$ or -COOH, and Ph represents $-C_6H_5$.

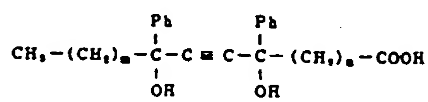
(Examples of acetylene diol derivatives)

No. 1



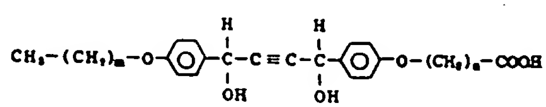
$30 \geq m + n \geq 11,\ n \geq 0$

No. 2



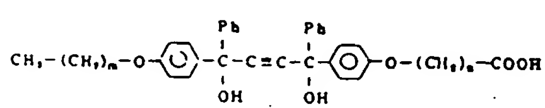
$30 \geq m + n \geq 11,\ n \geq 0$

No. 3



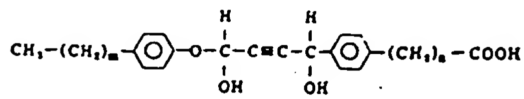
$30 \geq m + n \geq 8,\ n \geq 1$

No. 4



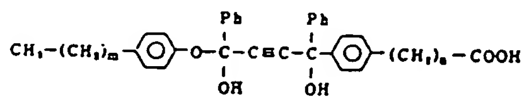
$30 \geq m + n \geq 8,\ n \geq 1$

No. 5



$30 \geq m + n \geq 8, \quad n \geq 0$

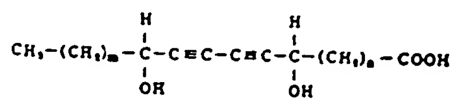
No. 6



$30 \geq m + n \geq 8, \quad n \geq 0$

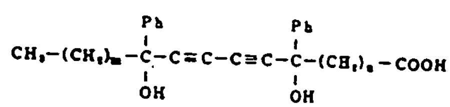
(Examples of diacetylene diol derivatives)

No. 7



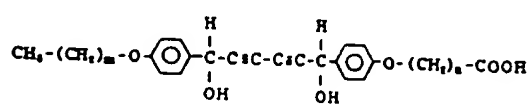
$30 \geq m + n \geq 9, \quad n \geq 0$

No. 8



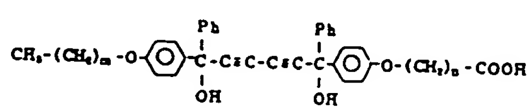
$30 \geq m + n \geq 9, \quad n \geq 0$

No. 9



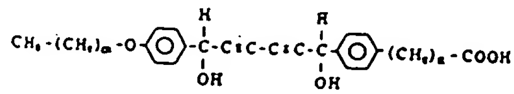
$30 \geq m + n \geq 5, \quad n \geq 1$

No. 10



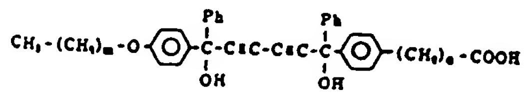
$30 \geq m + n \geq 5, \quad n \geq 1$

No. 11



$30 \geq m + n \geq 5,\ n \geq 0$

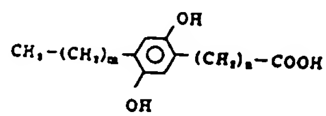
No. 12



$30 \geq m + n \geq 5,\ n \geq 0$

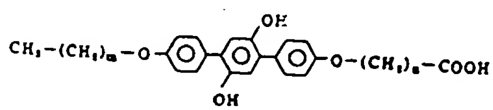
(Examples of hydroquinone derivatives)

No. 13



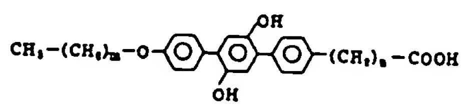
$30 \geq m + n \geq 13,\ n \geq 0$

No. 14



$30 \geq m + n \geq 9,\ n \geq 1$

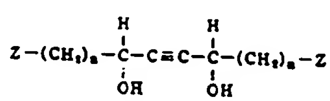
No. 15



$30 \geq m + n \geq 9,\ n \geq 0$

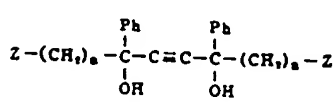
(Examples of acetylene diol derivatives)

No. 16



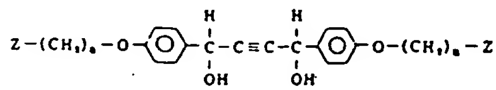
$30 \geq n \geq 5$

No. 17



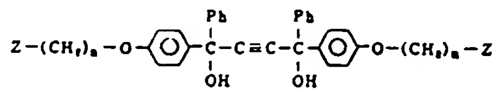
$30 \geq n \geq 5$

No. 18



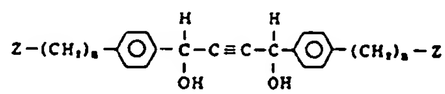
$30 \geq n \geq 4$

No. 19



$30 \geq n \geq 4$

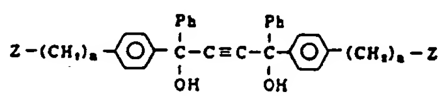
No. 20



$30 \geq n \geq 4$

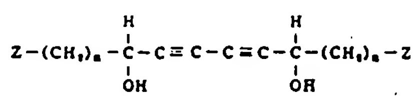
(Examples of diacetylene diol derivatives)

No. 21



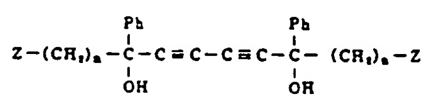
$30 \geq n \geq 4$

No. 22



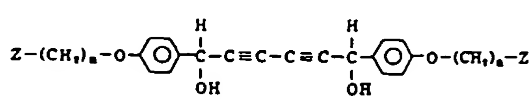
$30 \geq n \geq 3$

No. 23



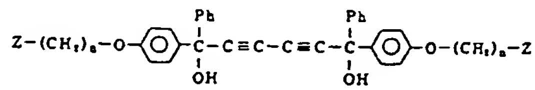
$30 \geq n \geq 3$

No. 24



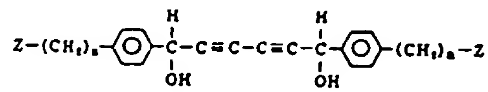
$30 \geq n \geq 1$

No. 25



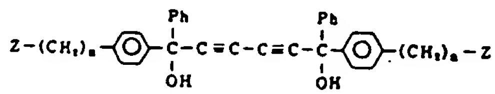
$30 \geq a \geq 1$

No. 26



$30 \geq a \geq 1$

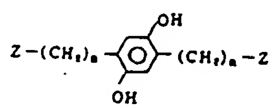
No. 27



$30 \geq a \geq 1$

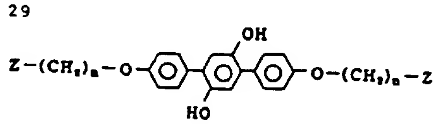
(Examples of hydroquinone derivatives)

No. 28



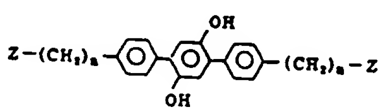
$30 \geq a \geq 5$

No. 29



$30 \geq a \geq 1$

No. 30



$30 \geq a \geq 1$

With the exception of the substitution of a long-chain alkyl group or long-chain carboxylic acid for the host molecule, and introducing hydrophilic properties or hydrophobic properties, the above-mentioned compounds themselves are known compounds; furthermore, formation of a crystalline inclusion complex of the

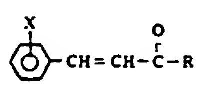
host molecule that is not modified with a long-chain alkyl group, etc. is also described in the Journal of the Chemical Society of Japan, No. 2, pp. 239-242 (1983).

For the guest molecule capable of producing an inclusion complex with the above-mentioned host molecules, in general, molecules capable of forming a strong hydrogen bond with the host molecule are desirable. For this reason, as described above, when the host molecule has a hydroxy group as the inclusion group, aldehyde, ketone, amine, sulfoxide, etc., can be mentioned as guests. Furthermore, for guest molecules, different types of halogen compounds, or π-electron type compounds, in other words, alkene, alkyne, arene, etc., can be selected. In either case, a molecule having a formula that makes it possible for the inclusion complex produced to have a desired image recording ability upon application of light.

For specific examples of guest molecules that can be used for recording media that utilize the photodimerization reaction of the guest molecule, olefin compounds (Nos. 31-34), diolefin compounds (Nos. 35-38), anthracene derivatives (No. 39), 2-aminopyridinium (No. 41), etc. can be mentioned.

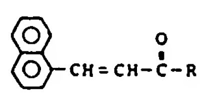
(Examples of olefin compounds)

No. 31



(X = -H , -o-CH_3, - p-CH_3
R = -H , -C_6H_5, -OH , -OCH_3)

No. 32



(R = -H , -C_6H_5, -OH , -OCH_3)

No. 33

NC-CH=CH-CN

No. 34

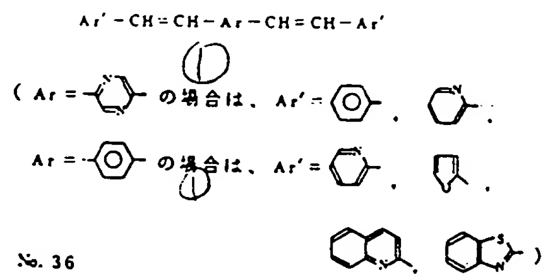
$R_1OOC-CH=CH-COOR_2$

($R_1 = R_2 = CH_3$ または $R_1 = CH_3$, $R_2 = H$)

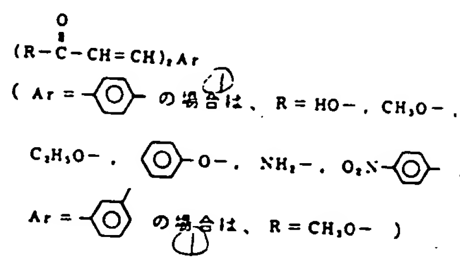
Key: 1 Or

(Examples of diolefin compounds)

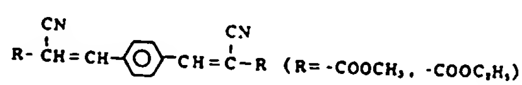
No. 35



No. 36



No. 37

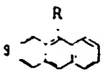


No. 38

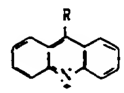
$R-CH=CH-\overset{O}{\overset{\|}{C}}-CH=CH-R$ ($R = C_6H_5$- , $-COOCH_3$)

Key: 1 In the case of

(Examples of anthracene derivatives)

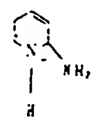
No. 39  ($R =$ CH_3-, CHO-, -$COOC_2H_5$, Br-)

(Examples of acridinium derivatives)

No. 40  $\cdot X^-$ ($R =$ -H, -CH_3, -C_2H_5, $X^- = I^-$, Br^-, Cl^-)

(2-Aminopyridinium)

No. 41

 $\cdot X^-$ ($X^- = Cl^-$, Br^-, I^-)

As a method of producing the monomolecular film or built-up monomolecular layer film of the inclusion complex comprised of the above-mentioned host molecules and guest molecules, for example, the Langmuir Project (LB method) developed by I. Langmuir et al. can be used. The LB method is a method in which a monomolecular film or built-up monomolecular layer film is produced by utilizing the tendency for molecules to form a monomolecular layer on the surface of water with the hydrophilic group facing downward when an appropriate balance is retained in a molecular formula having a hydrophilic group and hydrophobic group in the molecule (that is, balance of the two properties). The monomolecular layer on the surface of the water is a two-dimensional system. When the molecules are distributed

randomly, the equation of a two-dimensional ideal gas can be established between surface A and the surface tension Π per mole,

$$\Pi A = kT$$

and forms a "gaseous film." In this case, k is Boltzmann constant and T is the absolute temperature. When A is sufficiently reduced, the intramolecular interaction increases and forms a "condensed film (or solid film)" consisting of a two-dimensional solid material. The condensed film can be transferred to the surface of a carrier comprised of a different material or having a different shape, such as a glass base, one layer at a time. As a specific example of the method for producing the monomolecular film (which is referred to as a single complex molecular film), or single complex molecular built-up film of the host molecule that includes the guest molecule of the present invention; the five methods A-E shown below can be mentioned.

<A> The host molecule and the guest molecule of the target inclusion complex are dissolved in a solvent, it is then developed in an aqueous phase and the inclusion complex is precipitated in the form of a film. In this case, when the formula of the host molecule includes a hydrophilic group (carboxyl group) and a hydrophobic group (alkyl group) on both ends of the molecule as indicated by compound Nos. 1-15, the inclusion complex precipitated on the aqueous phase is developed on the aqueous phase with the hydrophilic group of the host molecule facing the aqueous phase regardless of the hydrophilic and hydrophobic properties of the guest molecule. On the other hand, when the host molecule takes on the formula indicated by

compound Nos. 16-30, Z = $-CH_3$ wherein both ends of the molecule consist of a hydrophobic group alone, the inclusion complex develops on the aqueous phase with the hydrophilic group of the guest molecule facing the aqueous phase as indicated by Figure 4. Also, in Z = -COOH wherein both ends of the molecule consisting of hydrophilic groups alone, the inclusion complex develops on the aqueous phase with the hydrophilic group of the host molecule facing the aqueous phase as indicated in Figure 5.

Subsequently, a partition board (or a float) is provided so that spreading of the precipitate on the aqueous phase does not occur freely, and the area of spreading is restricted, and the state of spreading of the film material is controlled, and the surface tension λ in proportion to the state of spreading is obtained. The partition board is then moved, and the area of spreading is reduced, the spreading of the film material is controlled, the surface tension is slowly increased, and a surface tension λ suitable for production of the built-up film can be obtained. The surface tension is retained, and the cleaned carrier is carefully placed in vertical motion, and the single complex molecular film is transferred to the carrier. The single complex molecular film is produced as described above, and the above-mentioned operation is repeated, single complex molecular built-up layer film with a desired degree of buildup can be produced.

In order to transfer the monomolecular layer onto the surface of the carrier, in addition to the above-mentioned dipping method, the horizontal adsorption method, rotational cylinder method, etc., can be mentioned. The horizontal

adsorption method is a method in which the carrier is brought into contact with the surface of the water horizontally and the transfer is carried out, and the rotational cylinder method is a method in which a cylindrical carrier is rotated on the surface of the water, and the monomolecular layer is transferred to the surface of the carrier. In the above-mentioned vertical dipping method, a monomolecular layer with the hydrophilic group of the host molecule facing the carrier side can be produced when a carrier with a surface having hydrophilic properties is pulled out of the water in a direction crossing the surface of the water. When the carrier is transported in the vertical direction as described above, a single monomolecular layer is built up for each process. The position of the film molecules produced is reversed in the removal process and dipping process; therefore, when the above-mentioned method is used, a Y-type film, in which the hydrophilic group and hydrophilic group of the host molecule and hydrophobic group and hydrophobic group of the host molecule face each other between the layers, can be produced. On the other hand, in the horizontal adsorption method, the carrier is brought into contact with the surface of the water, and the transfer is carried out, and a single complex molecular layer with the hydrophobic group of the host molecule facing the carrier side can be produced on the carrier. In said method, a change in the direction of the film molecules produced does not occur even when built up, and an X-type film, in which the hydrophobic group faces the carrier in all layers can be produced. And a built-up film in which the hydrophilic group faces the carrier side in all layers is referred to as a Z-type film.

In the rotational cylinder method, a cylindrical carrier is rotated on the surface of the water, and the monomolecular layer is transferred to the surface of the carrier. Transferring the monomolecular layer onto the carrier is not limited to the above-mentioned methods, and when a carrier with a large surface area is used, a method in which the carrier is extruded into the aqueous phase from a carrier roll, etc., can be used as well. Also, the orientation of the hydrophilic group or hydrophobic group facing the carrier described above is a rule, and a surface treatment can be provided for the carrier, and the direction can be changed.

In the above-mentioned film formation process, control of the orientation in the in-plane direction of the film material has been mainly controlled through adjustment of the surface tension in the past, but it has been very difficult to achieve a highly ordered orientation unless the film material is a compound with a very simple formula, for example, a straight-chain fatty acid, etc. However, in the present invention, an inclusion complex is used as a film material, thus, a film with a highly ordered orientation can be produced relatively easily. In other words, the configuration between the host molecule-guest molecule, host molecule-host molecule, and guest molecule-guest molecule are defined at the point where the inclusion complex is precipitated on the aqueous phase based on the hydrogen bonds, van der Waals force, etc., and the host molecule and guest molecule are arranged with a crystal lattice order. Also, when the guest molecule alone has the function, chemical modification for the guest molecule, in other words, introduction of a hydrophobic group or hydrophilic group is not performed, thus, a

reduction in the function accompanied by film formation does not occur.

<B> A guest molecule that exhibits solubility is dissolved in the aqueous phase. Subsequently, a host molecule is dissolved with a solvent and spread on the aqueous phase. In this case, formation of the inclusion complex takes place between the host molecule-guest molecule at the same time, and formation of a film takes place. The combination of the host molecule and guest molecule and the film formation method that follows are based on the methods described in <A>.

<C> A guest molecule that exhibits solubility is dissolved in the aqueous phase. Subsequently, the host molecules and guest molecules of the target inclusion complex are dissolved in a solvent and spread on the aqueous phase. The combination of the host molecule and guest molecule and the film formation method that follows are based on the method described in <A>.

<D> A host molecule is dissolved in a solvent and spread on the aqueous phase. Subsequently, a closed system device is used and the side of the gaseous phase, that is, a gas atmosphere of the guest molecule is formed in the space inside the device. In this case, the guest molecule on the gaseous phase side is included at the same time, and an inclusion complex is precipitated in a form of a film. The above-mentioned method is especially effective for compounds in which the guest molecule has a low boiling point and is likely to vaporize, for example, acetone, etc. The combination of the host molecule and guest molecule and the film formation method that follows are based on the method described in <A>.

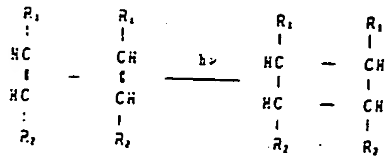
<E> A closed system device is used and the side of the gaseous phase, that is, the space inside the device is filled with a gas atmosphere comprised of the guest molecule. Then, the host molecule and guest molecule of the target inclusion complex are dissolved in a solvent, it is then sprayed onto the aqueous phase and an inclusion complex is precipitated in the form of a film. The combination of the host molecule and guest molecule, and the film formation method that follows are based on the method described in <A>.

The single complex molecular film and single complex molecular built-up film produced on the carrier using the above-mentioned methods have a high density and highly ordered orientation, and when a recording layer is made with the above-mentioned films, a recording medium having good characteristics as a high-density, high-resolution recording medium, which can be used for optical recording, thermal recording, electrical recording, magnetic recording, etc., can be produced.

When the single complex molecular film and single complex molecular built-up film produced above are used as the recording layer of a recording medium, a variety of recording methods, as described below, are conceivable.

Optical recording medium that utilizes the photodimerization reaction of the guest molecule, for example, when one of Nos. 7-15 and Nos. 22-30 is used for the host molecule, and a guest molecule having a photodimeric double bond such as those indicated by No. 31-38 are used in combination, an inclusion complex having a host molecule and guest molecule composition ratio (mole ratio) of 1:2 can be produced. When the energy

required to achieve polymerization, such as gamma rays, X-rays, or ultraviolet light is applied to the above-mentioned single complex molecular film or single complex molecular layer built-up film according to a specified pattern, dimerization takes place between the guest molecules in the irradiated areas, as indicated by equation III.



(III)

The above-mentioned reaction can occur when the distance between adjoining unsaturated bonds is 4 Å or less, but in a single complex molecular film or single complex molecular layer built-up film produced by the above-mentioned methods, not only can the dimerization product be produced easily, but also, only one type of isomer or formula among a variety of materials that are likely to be produced at the time of the dimerization reaction can be produced. In other words, the configuration between the guest molecules in the inclusion complex layer is very orderly. Also, depolymerization does not occur after dimerization even in the dark, and areas that are note exposed to radiation remain in the monomer form; thus, a recording based on a specified pattern can be produced as indicated by Figure 1.

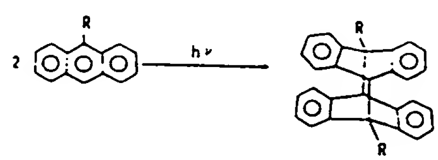
Reading of the recorded information can be done by, for example, radiation or visible light. In other words, the conjugated system of the monomer undergoes decomposition when polymerization is performed; thus, changes occur in the absorption wavelength of the visible light. The maximum absorption wavelength shifts toward the lower wavelengths; thus,

playback of the information can be achieved by reading the change in spectral absorption (Figure 2).

In addition to reading the spectral absorption by visible light, playback can be achieved by reading the change in volume and after dimerization using the schlieren method. The above-mentioned method is especially effective when a single complex molecular film or single complex molecular built-up film of a compound having a formula that exhibits a significant difference in volume at the time of polymerization and after the dimerization. Also, instead of directly forming the single complex molecular film or single complex molecular layer built-up film on the base, an optically conductive layer, such as Se, ZnO, and CdS, can be produced on the base, and a single complex molecular film or single complex molecular layer built-up film is also produced; thus, the difference in absorption between the monomer and the dimer can be read electronically.

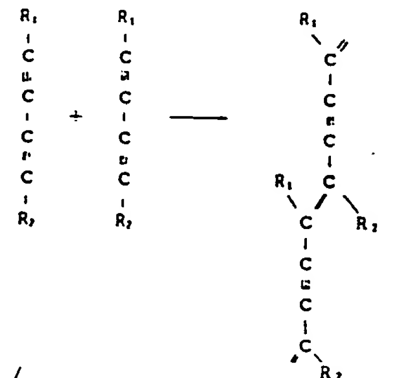
The dimer has absorption at a wavelength of 270 nm based on the cyclobutane ring, and when ultraviolet light with a wavelength of 270 nm is applied, the dimer returns to the initial two monomer molecules. Thus, erasure of the recorded information is possible (Figure 3).

Also, as the guest molecule of the photodimer, a compound such as the anthracene derivatives indicated by No. 39 can be used. In this case, the photodimerization reaction progresses according to reaction equation IV.



(IV)

Also, when No. 7 is used as the host molecule, polymerization takes place between host molecules in the irradiated areas as indicated by equation V when the energy required for polymerization such as X-rays, gamma rays, and ultraviolet light is applied, and polydiacetylene is produced.



(V)

$$\left(R_1 = CH_3-(CH_2)_m-\underset{OH}{\overset{H}{C}}- \ , \ R_2 = HOOC-(CH_2)_n-\underset{OH}{\overset{H}{C}}- \quad 30 \geq m+n \geq 9,\ n \geq 0 \right)$$

Therefore, a significant increase in the adhesion with the base is made possible when a total exposure is performed for the single complex molecular film or single complex molecular built-up film. In particular, a significant increase in the chemical resistance (solvent resistance) can be observed. When the above-mentioned total exposure is performed, when the guest molecule has photodimeric properties, dimerization also takes place in the guest molecule, but when the material is used as an optical recording medium, as a case opposite the example described above, when depolymerization is performed through application of light with a wavelength at the absorption

wavelength of the cyclobutane ring (ultraviolet light) according to a specified pattern, recording or display can be achieved.

For the above-mentioned optical recording medium, one with a film thickness of 100-3000 Å is especially desirable.

As indicated by the principle, the method for producing the film is very simple, and it is possible to produce a recording medium with the above-mentioned superior properties at low cost.

The carrier used for production of the above-mentioned single complex molecular film or single complex molecular built-up film used in the present invention is not especially limited, but when a surfactant is adsorbed on the surface of the carrier, the single complex molecular film is disturbed when the single complex molecular layer film is transferred from the surface of water, and a high-quality single complex molecular film or single complex molecular layer built-up film cannot be produced; thus, a carrier with a clean surface is used. Examples of carriers that can be used in this case include, glass, metals such as aluminum, plastics, ceramics, etc.

The single complex molecular film or single complex molecular built-up film formed on the carrier is firmly bonded, and peeling or delamination from the carrier hardly occurs, but in order to further increase the adhesion, an adhesive layer can be formed between the single complex molecular film or single complex molecular built-up film and the carrier. Also, the adhesion can be increased through selection of the conditions of formation of the single complex molecular layer film, for example, concentration of the hydrogen ion in the aqueous phase, type of ion used, water temperature, carrier transport speed, etc.

It is desirable to provide a protective film on the single complex molecular film or single complex molecular built-up film from the standpoint of chemical stability of the single complex molecular film or single complex molecular built-up film, but depending on the type of film-forming molecule, a protective film is not a requirement.

In the following, the present invention is further explained in specific terms with application examples. Compound Nos. 49-54 are listed in Table I.

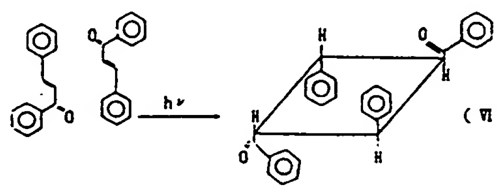
Application Example 1

An optical recording medium that utilizes the photodimerization reaction of the guest molecule (1)

Diacetylene diol indicated by No. 49 was used as a host molecule, and chalcone was used as the guest molecule and the two were dissolved in chloroform at a mole ratio of 1:2, and spread over an aqueous phase of cadmium chloride with a pH of 6.5 and concentration of 4×10^{-4}M. After removing the chloroform solvent by evaporation, the surface tension was increased to 35 dyne/cm, and precipitation of the inclusion complex was performed in the form of a film. Subsequently, the surface tension was kept constant, a glass board with a thoroughly clean surface having hydrophilic properties was gently moved in the vertical direction at a rate of 7 cm/min such that the board crossed the surface of the water, and a single complex molecular film was transferred to the board, and a single complex molecular film, and an optical recording medium having a recording layer comprised of a single

complex molecular film, and a single complex molecular built-up film formed by buildup of 3, 5, 9, 15, and 19 layers were produced. In the above-mentioned buildup process, the board was left standing for 30 min each time after being removed from the aqueous phase, and the moisture adsorbed on the board was removed by evaporation. As for the film formation machine, a Langmuir-Trough 4 produced by Joyce Corp. of England was used.

X-ray application was done for the optical recording medium produced according to a pattern, and the dimerization reaction of the guest molecule indicated by equation VI was performed, and information recording was performed. A high-density recording on the molecular level was possible.



(VI)

Chalcone

Playback of the recording was performed by reading the change in absorption at a wavelength of around 380-420 nm associated with dimerization of the guest molecule. Subsequently, when ultraviolet light was applied at a wavelength of 270 nm for 1 h, depolymerization took place, and the recording was erased.

Application Examples 2-12

Instead of the chalcone described in Application Example 1, compounds indicated by Nos. 31-38 were used as guest molecules, and similar results were obtained. (Application Examples 2-9)

Furthermore, when chalcone was used as the guest molecule, and compounds indicated by Nos. 50-52 were used as host molecules, recording, playback, and furthermore, erasure of the recording were made possible as in Application Example 1. (Application Examples 10-12)

Application Examples 13-24

Optical recording medium that utilizes optical dimerization reaction of the guest molecule (2)

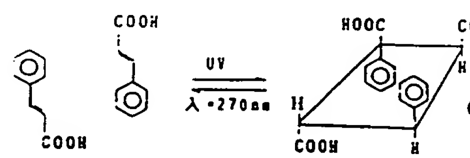
First, total exposure was performed for each optical recording medium described in Application Examples 1-12 using a high-pressure tension mercury lamp, and dimerization was performed for all of the guest molecules. Ultraviolet light with a wavelength of around 270 nm, which corresponds to the maximum absorption of the cyclobutane ring produced at the time of dimerization, was applied to the above-mentioned media to form a pattern, depolymerization of the guest molecule was carried out, and information recording was performed. Recording on the molecular level was possible. Playback was accomplished by reading the change in absorption at wavelengths of approximately 380-420 nm associated with the depolymerization of the guest molecule. It was confirmed that erasure of the recording, that is, dimerization of all of the guest molecules, was possible by

means of total exposure of the above-mentioned recording medium with a high-pressure mercury lamp.

Application Example 25

An optical recording medium that utilizes optical dimerization of guest molecule (3)

Diacetylene diol indicated by No. 53 was used as the host molecule, and cinammic acid was used as the guest molecule, and optical recording media with a recording layer comprised of a single complex molecular film, and built-up layers of 3, 5, 9, 15, and 19 layers were produced as in Application Example 1. Subsequently, total exposure was performed for the above-mentioned films with a high-pressure mercury lamp, and dimerization of the guest molecule (equation VII) was carried out, and polymerization of the host molecule (equation V) was carried out; subsequently, ultraviolet light with a wavelength of 270 nm was applied according to a specified pattern, depolymerization of the guest molecule was performed, and information recording was accomplished. Recording on the molecular level was made possible.



(VII)

Playback was accomplished by reading the change in absorption at wavelengths of approximately 380-420 nm associated with the depolymerization of the guest molecule.

Subsequently, it was confirmed that erasure of the recording was possible by means of a total exposure of the above-mentioned recording medium with a high-pressure mercury lamp. Also, the recording medium that had been totally exposed with a high-pressure mercury lamp was dipped in alcohol for approximately 30 sec and recording/playback of information was performed as described above, and no problems were observed. In other words, it was confirmed that the chemical resistance of the recording medium can be increased when polymerization is performed for the host molecule.

Application Examples 26 and 27

Diacetylene diol indicated by No. 53 was used as the host molecule, and anthraaldehyde was used as the guest molecule and it was dissolved in chloroform at a mole ratio of 1:2 and an optical recording media with recording layers comprised of a single complex molecular film, and built-up layers of 5, 9, 15, 31, 60, and 80 layers were produced as in Application Example 1.

Subsequently, X-ray radiation was performed for the optical recording medium produced, and the dimerization indicated by equation (IV) of the guest molecule was carried out, and information recording was performed. Recording on the molecular level was possible. Playback was performed by reading the change in absorption at wavelengths of approximately 370-390 nm associated with dimerization of the guest molecule. When ultraviolet light with a wavelength of 313 nm was applied for 1 h, depolymerization took place, and it was confirmed that erasure of the recording was possible.

Similar results were obtained when the anthracene derivative indicated by No. 41 was used. (Application Example 27)

Table I

	1 基本骨格	
No.49	No.10	m = 9 . n = 2
No.50	No.25	Z=COOH. n = 2
No.51	No.15	m = 9 . n = 2
No.52	No.30	Z=COOH. n = 4
No.53	No.7	m = 8 . n = 8
No.54	No.4	m = 9 . n = 2

Key: 1 Base skeleton

<u>Brief explanation of figures</u>

Figures 1-3 show vertical cross sections for explaining application examples of the recording medium of the present invention. Figure 1 shows the recording process, Figure 2 shows the playback process, and Figure 3 shows the erasure process, respectively. Figures 4-5 are explanatory diagrams showing the state of the inclusion complex of the present invention at the aqueous phase interface.

1...Host molecule
2...Guest molecule

3...Hydrophilic group
4...Long-chain alkyl group
5...Base
6...X-ray
7...Dimerized group
8...Visible light
9...Ultraviolet light
10, 11...Inclusion complex group
12, 13...Non-inclusion complex group
14...Long-chain fatty acid group
15...Hydrophobic group
16...Aqueous phase

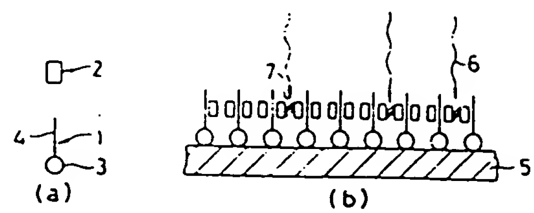


Figure 1

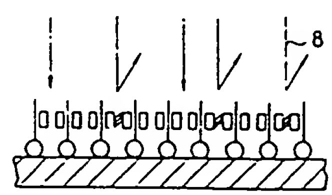


Figure 2

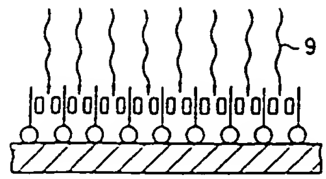


Figure 3

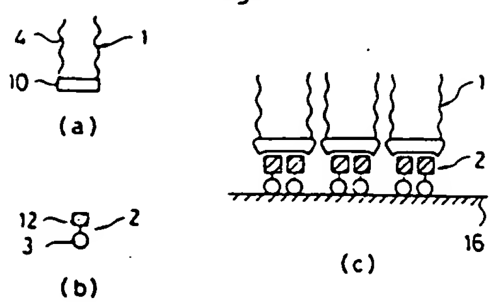


Figure 4

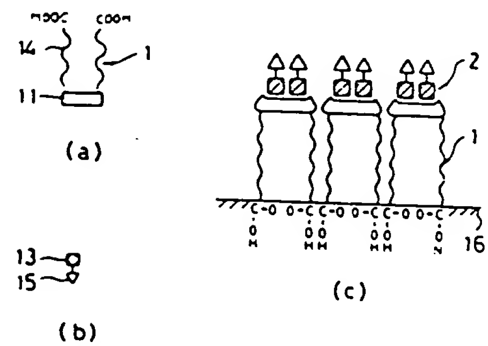


Figure 5

⑲日本国特許庁（JP）　　⑪特許出願公開

⑫公開特許公報（A）　　昭60-239740

⑤Int.Cl.⁴	識別記号	庁内整理番号	㊸公開　昭和60年(1985)11月28日
G 03 C 1/72		8205-2H	
G 11 B 7/24		A-8421-5D	

審査請求　未請求　発明の数　1　（全12頁）

⑭発明の名称　記録媒体

㉑特　願　昭59-95572
㉒出　願　昭59(1984)5月15日

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明　細　書

1.発明の名称

記録媒体

2.特許請求の範囲

その分子内に親水性部位、疎水性部位及び包接部位を有するホスト分子と該ホスト分子に包接されるゲスト分子とからなる包接錯体の単分子膜又は単分子層累積膜を担体上に形成して記録層とし、光により記録を行なうことを特徴とする記録媒体。

3.発明の詳細な説明

(1) 技術分野

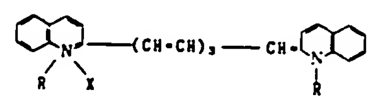
本発明は、包接錯体の単分子膜、乃至単分子層累積膜の化学変化若しくは物理変化を利用して記録を行なう記録媒体に関する。

(2) 背景技術

従来、有機化合物を記録層とする記録媒体としては種々のものが知られている。

例えば、有機化合物を薄膜にして記録層として用いる光記録媒体については、例えば特開昭56-16948号公報、特開昭58-125246号公報にも開示されている。いずれも有機色素を記録層とし、レーザビームにより記録再生を行なうレーザ記録媒体に関するものである。特に、特開昭58-125246号公報に開示された媒体は、

一般式（I）


（I）

で表わされるシアニン系色素の薄膜を記録層とするものである。（I）式で表わされるシアニン系色素溶液を回転塗布機などを用いて、1000Å以下の厚さ、例えば約300Åの厚さにプラスチック基板上に塗布し薄膜を形成する。膜内の分子分布配向がランダムであると、光照射に伴って膜内で光の散乱が生じ、微視的にみた場合各光照射の度に生ずる化学反応の度合が異なってくる。そこで記録媒体としては、膜内の分子分布、配向が一様になっていることが望ましく、またできる限り膜厚が薄いことが、記録の高密度化のために要請され

る。しかしながら、塗布法による場合、膜厚においては300Å程度が限界であり、膜内の分子分布、配向がランダムであることは解決しがたいことであった。

レジスト材料の一つとして光量子効率が大でかつ優れた解像力を有するものとして提案されていたジアセチレン化合物累積膜が、レジスト材料のみならず、薄膜電気－光学デバイス、電気－音響デバイス、圧・焦電デバイス等にも応用されることが、特開昭56-42229号公報、特開昭58-43220号公報などに示されている。

近時においては、ジアセチレン化合物累積膜の製造方法の改良について特開昭58-111029号公報に示されている。かかる発明にて製造された基板上のジアセチレン化合物累積膜は紫外線を照射することにより重合させてジアセチレン化合物重合体膜を作り、或はマスキングして紫外線を照射し部分的に重合させ、未重合部分を除去して図形を作り、薄膜光学デバイスや集積回路素子として使用される。

しかし、これらはいずれもジアセチレン化合物に限るものであり、薄膜光学デバイスとして使用するときに、一度記録したものの消去の可能性については述べられていない。

一方、上述欠点を解決すべく、分子内に親水基、疎水基及び少なくとも1個の不飽和結合を有する1種類の光重合性モノマーの単分子膜又は単分子層累積膜を基板上に形成して記録層としたことを特徴とする、反復使用可能な光記録媒体が特開昭58-190932号の光記録媒体に示されている。

これらのジアセチレン化合物累積膜にしても、光重合性オレフィンモノマーの単分子膜若しくは単分子層累積膜にしても、光反応性化合物に親水基、疎水基を導入して、直接基板上に担持させる製法を採用している。従って、種々の機能性膜を簡単に作製することが困難なのに加えて、親水基、疎水基の導入に伴う光反応性の低下の恐れがあった。更には、非常に高度な高密度記録を行う際に重要となる、膜面内の分子配向の制御についても、極めて複雑な操作が要求される問題があった。

かかる従来例の欠点を解消し、1)各種の機能性膜を比較的簡単に作製する方法、2)その際、機能性分子の持つ各種機能が、薄膜化した場合に於いても、損失若しくは低下されることなく発現する様に膜化する方法、更には、3)上記の薄膜化に於いて、特別な操作を行うことなしに、膜構成分子が膜面内方向に対して、高度の秩序構造を持って配向される方法を種々検討した結果、本発明を成すに至った。又、かかる成膜法を用いて、高密度、高解像度の記録媒体を、容易にかつ高品質に提供できるに至った。

(3) 発明の開示

本発明の目的は、光により分子単位での化学変化若しくは物理変化を起こす様な高密度記録媒体を提供することにある。

また、この様な分子単位での高密度記録を行うのに際して重要な因子となる媒体面内での分子配向に関して、従来例よりも秀逸な媒体を提供することにある。更には、上述記録媒体を製造するに当って、比較的簡単な操作変更により、様々な性質を有する媒体を提供することにある。

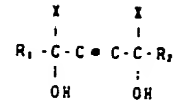
本発明の上記目的は、以下の本発明によって達成される。

その分子内に親水性部位、疎水性部位及び他分子との包接が可能な部位（包接部位）を有する分子（ホスト分子）と該ホスト分子に包接される別種の分子（ゲスト分子）とからなる包接錯体の単分子膜又は単分子層累積膜を担体上に形成して記録層とし、光により記録を行なうことを特徴とする記録媒体。

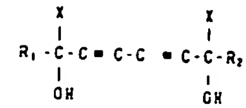
本発明の記録層を構成する物質は、分子内に親水性部位、疎水性部位及び他分子との包接が可能な部位を少なく共1ヶ所有する分子（これをホスト分子と呼ぶ）と該ホスト分子に包接される別種の分子（これをゲスト分子と呼ぶ）の二種の分子からなる。かかるホスト分子とゲスト分子とからなる包接錯体の単分子膜、乃至単分子層累積膜を担体上に形成することにより、本発明の記録媒体が形成される。但し、これら二種類の分子の内、

どちらか一方、若しくは、両方が、光により、化学変化若しくは物理変化を起こすことが必要である。即ち、本発明における記録媒体は、前述の化学変化や物理変化を利用して記録を行なう。

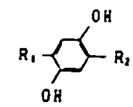
本発明に用いられるホスト分子としては、上述の如く、分子内の適当な位置に親水性部位、疎水性部位及び少なく共1ヶ所の他種分子との包接錯体を形成可能な部位を有する分子であれば広く使用することができる。分子内に親水性部位や疎水性部位を形成し得る構成要素としては、一般に広く知られている各種の親水基や疎水基等が代表的なものとして挙げられる。他種分子との包接錯体を形成し得る部位は、水酸基、カルボニル基、カルボキシル基、エステル基、アミノ基、ニトリル基、チオアルコール基、イミノ基等の導入によって形成される。このようなホスト分子を、一般式(Ⅱa)～(Ⅱc)で示される水酸基を持つホスト分子を例として、以下に具体的に説明する。



(Ⅱa)



(Ⅱb)



(Ⅱc)

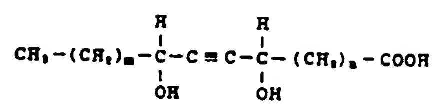
(ここで、X=H またはC_6H_5である。)

すなわち、分子内に親水性部位および疎水性部位を有するとは、例えば上式に於いてR_1部及びR_2部の何れか一方に親水性部位が存在し、他方に疎水性部位が存在するか、R_1部及びR_2部が両部以外の残りの部との関係に於いて共に親水性、若しくは疎水性を示すことを言う。R_1部及び、R_2部の構造に関して、疎水性部位を導入する場合には特に炭素原子数 5～30の長鎖アルキル基が、又親水性部位を導入する場合には特に炭素原子数 1～30の脂肪酸が望ましい。

本発明におけるホスト分子を更に具体的に示せば、例えば以下に列挙するアセチレンジオール誘導体(No.1～No.6、No.16～No.21)、ジアセチレンジオール誘導体(No.7～No.12、No.22～No.27)、ハイドロキノン誘導体(No.13～No.15、No.28～No.30)等が利用し得るものとして挙げられる。尚、以下の例における m、nは、正の整数を、Zは、$-CH_3$または $-COOH$を、Phは、$-C_6H_5$を示すものとする。

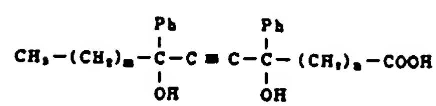
(アセチレンジオール誘導体の例)

No. 1



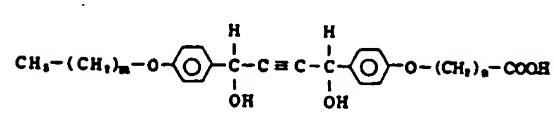
$30 \geq m+n \geq 11,\ n \geq 0$

No. 2



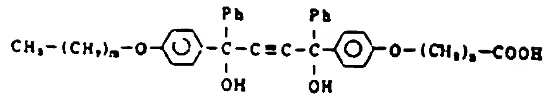
$30 \geq m+n \geq 11,\ n \geq 0$

No. 3



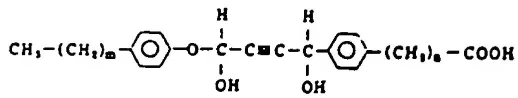
$30 \geq m+n \geq 8,\ n \geq 1$

No. 4



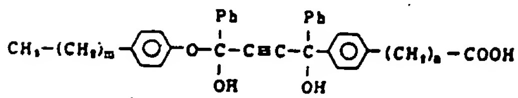
$30 \geqq m+n \geqq 8,\ n \geqq 1$

No. 5



$30 \geqq m+n \geqq 8,\ n \geqq 0$

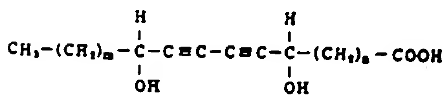
No. 6



$30 \geqq m+n \geqq 8,\ n \geqq 0$

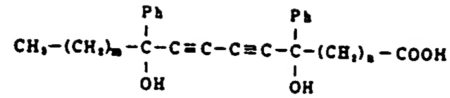
〔ジアセチレンジオール誘導体の例〕

No. 7



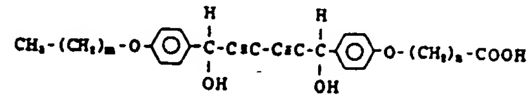
$30 \geqq m+n \geqq 9,\ n \geqq 0$

No. 8



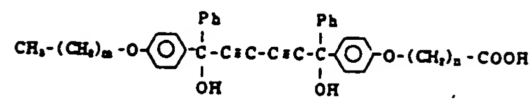
$30 \geqq m+n \geqq 9,\ n \geqq 0$

No. 9



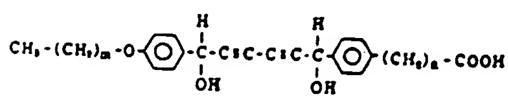
$30 \geqq m+n \geqq 5,\ n \geqq 1$

No. 10



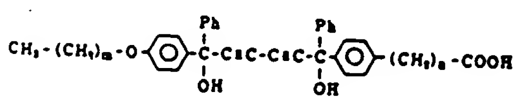
$30 \geqq m+n \geqq 5,\ n \geqq 1$

No. 11



$30 \geqq m+n \geqq 5,\ n \geqq 0$

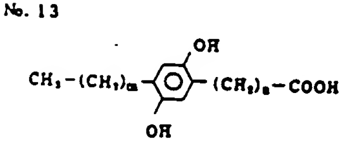
No. 12



$30 \geqq m+n \geqq 5,\ n \geqq 0$

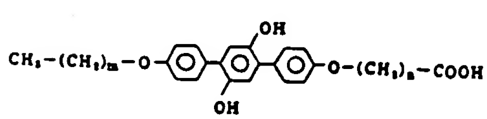
〔ハイドロキノン誘導体の例〕

No. 13



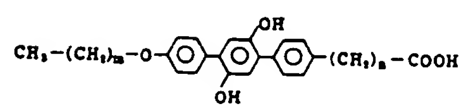
$30 \geqq m+n \geqq 13,\ n \geqq 0$

No. 14



$30 \geqq m+n \geqq 9,\ n \geqq 1$

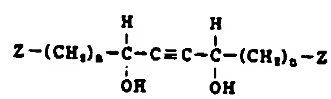
No. 15



$30 \geqq m+n \geqq 9,\ n \geqq 0$

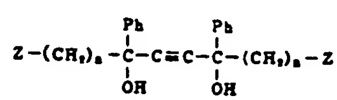
〔アセチレンジオール誘導体の例〕

No. 16



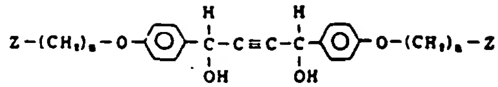
$30 \geqq n \geqq 5$

No. 17



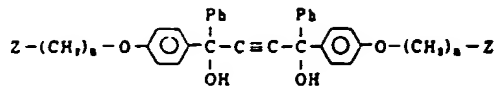
$30 \geqq n \geqq 5$

No. 18



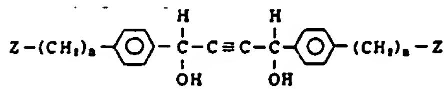
$30 \geqq n \geqq 4$

No. 19



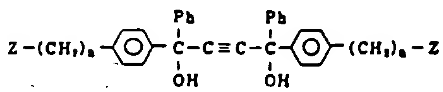
$30 \geqq n \geqq 4$

No. 20



$30 \geqq n \geqq 4$

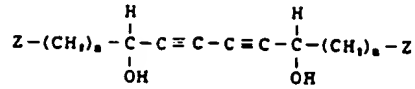
No. 21



$30 \geqq n \geqq 4$

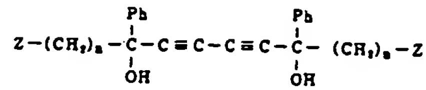
〔ジアセチレンジオール誘導体の例〕

No. 22



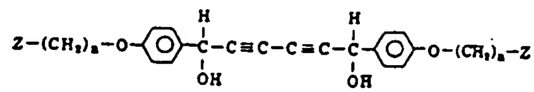
$30 \geqq n \geqq 3$

No. 23



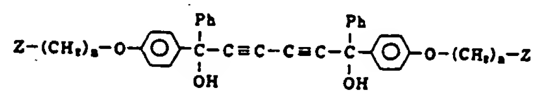
$30 \geqq n \geqq 3$

No. 24



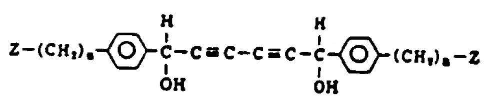
$30 \geqq n \geqq 1$

No. 25



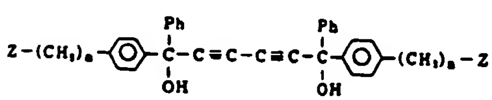
$30 \geqq n \geqq 1$

No. 26



$30 \geqq n \geqq 1$

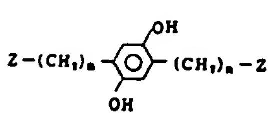
No. 27



$30 \geqq n \geqq 1$

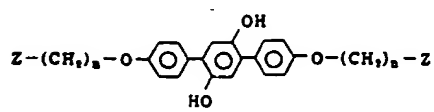
〔ハイドロキノン誘導体の例〕

No. 28



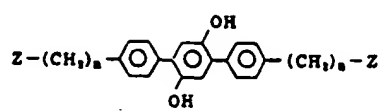
$30 \geqq n \geqq 5$

No. 29



$30 \geqq n \geqq 1$

No. 30



$30 \geqq n \geqq 1$

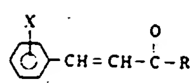
以上挙げた化合物はホスト分子に長鎖アルキル基や長鎖カルボン酸等を置換させて親水性や疎水性を導入した点を除けばそれ自体既知の化合物であり、又、長鎖アルキル基等で修飾されていないホスト分子が、種々のゲスト分子と結晶性の包接錯体を形成する点に関しても、日本化学会誌No.2 229頁-242頁（1983年）に述べられている。

これらホスト分子と包接錯体を作り得るゲスト分子としては、一般に、ホスト分子と強い水素結合を形成し得る分子が望ましい。従って、先に述べた如く、ホスト分子が包接部位として水酸基を有する場合には、ゲスト分子として、アルデヒド、ケトン、アミン、スルフォキシド等を挙げることができる。また、ゲスト分子としては他に、各種ハロゲン化合物、或いはπ-電子系化合物、即ちアルケン、アルキン、及びアレーン等を選ぶ事もできる。何れにせよ、形成される包接錯体が光により所望の記録をすることのできる分子が選ばれる。

例えばゲスト分子の光二量化反応を用いた記録媒体に利用し得るゲスト分子の具体例としては、オレフィン化合物（No.31～No.34）、ジオレフィン化合物（No.35～No.38）、アントラセン誘導体（No.39）、2-アミノピリジニウム（No.41）等が挙げられる。

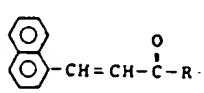
〔オレフィン化合物の例〕

No. 31



（$X = -H, -o-CH_3, -p-CH_3$, $R = -H, -C_6H_5, -OH, -OCH_3$）

No. 32



（$R = -H, -C_6H_5, -OH, -OCH_3$）

No. 33

$NC-CH=CH-CN$

No. 34

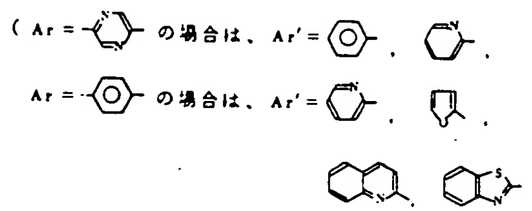
$R_1OOC-CH=CH-COOR_2$

（$R_1 = R_2 = CH_3$ または $R_1 = CH_3$、$R_2 = H$）

〔ジオレフィン化合物の例〕

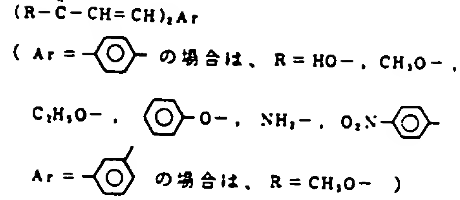
No. 35

$Ar'-CH=CH-Ar-CH=CH-Ar'$

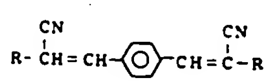


No. 36

$(R-\overset{O}{\overset{\|}{C}}-CH=CH)_2Ar$



No. 37

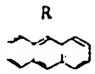


（$R = -COOCH_3, -COOC_2H_5$）

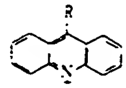
No. 38

$R-CH=CH-\overset{O}{\overset{\|}{C}}-CH=CH-R$ （$R = C_6H_5-, -COOCH_3$）

〔アントラセン誘導体の例〕

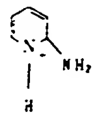
No.39  (R= CH_3-, CHO-, -$COOC_2H_5$, Br-)

〔アクリジニウム誘導体の例〕

No.40  ・X^- (R=-H, -CH_3, -C_2H_5
X^-=I^-, Br^-, Cl^-)

〔2-アミノピリジニウム〕

No.41

 ・X^- (X^-=Cl^-, Br^-, I^-)

このようなホスト分子およびゲスト分子から成る包接錯体の単分子膜または単分子層累積膜を作成する方法としては、例えばI.Langmuirらの開発したラングミュア・ブロジェット法(LB法)を用いる。LB法は、例えば分子内に親水基と疎水基を有する構造の分子において、両者のバランス(両親媒性のバランス)が適度に保たれているとき、分子は水面上で親水基を下に向けて単分子の層になることを利用して単分子膜または単分子層の累積膜を作成する方法である。水面上の単分子層は二次元系の特徴をもつ。分子がまばらに散開しているときは、一分子当り面積Aと表面圧Πとの間に二次元理想気体の式、

$$\Pi A = kT$$

が成り立ち、"気体膜"となる。ここに、kはボルツマン定数、Tは絶対温度である。Aを十分小さくすれば分子間相互作用が強まり二次元固体の"凝縮膜(または固体膜)"になる。凝縮膜はガラス基板などの種々の材質や形状を有する担体の表面へ一層ずつ移すことができる。この方法を用いて、本発明のゲスト分子を包接するホスト分子の単分子膜(これを単錯体分子膜と呼ぶことにする)、若しくは単錯体分子層累積膜の具体的な製法としては、例えば以下に示すA～Eの5法を挙げることができる。

〔A〕目的とする包接錯体のホスト分子とゲスト分子とを溶剤に溶解し、これを水相上に展開させて包接錯体を膜状に析出させる。この場合、ホスト分子の構造がNo.1～No.15に示したような分子の両端に親水性部位(カルボキシル基)と疎水性部位(アルキル基)を併有するものであれば、水相上に析出する包接錯体はゲスト分子の親水性および疎水性のいかんにかかわらず、ホスト分子の親水性部位を水相に向けた状態で水相上に展開する。一方、ホスト分子がNo.16～No.30に示した構造をとる場合、分子の両端が疎水性部位のみで構成される Z=-CH_3 は、水相上に析出する包接錯体は、ゲスト分子の親水性部位を水相に向けた第4図に示すような状態で水相上に展開する。又、分子の両端が親水性部位のみで構成される Z=-COOH では水相上に形成される包接錯体は、ホスト分子の親水性部位を水相に向けた第5図に示すような状態で水相上に展開する。

次にこの析出物が水相上を自由に拡散して広がりすぎないように仕切板(または浮子)を設けて展開面積を制限して膜物質の集合状態を制御し、その集合状態に比例した表面圧Πを得る。この仕切板を動かし、展開面積を縮少して膜物質の集合状態を制御し、表面圧を徐々に上昇させ、累積膜の製造に適する表面圧Πを設定することができる。この表面圧を維持しながら静かに清浄な担体を垂直に上下させることにより単錯体分子膜が担体上に移しとられる。単錯体分子膜は以上で製造されるが、単錯体分子層累積膜は前記の操作を繰り返すことにより所望の累積度の単錯体分子層累積膜が形成される。

単錯体分子層を担体上に移すには、上述した垂直浸せき法の他、水平付着法、回転円筒法などの方法による。水平付着法は担体を水面に水平に接触させて移しとる方法で、回転円筒法は、円筒型の担体を水面上を回転させて単錯体分子層を担体表面に移しとる方法である。前述した垂直浸せき法では、表面が親水性である担体を水面を横切る方向に水中から引き上げるとホスト分子の親水基が担体側に向いた単錯体分子層が担体上に形成される。前述のように担体を上下させると、各行程ごとに1枚ずつ単錯体分子層が積み重なってい

く、成膜分子の向きが引上げ行程と沈せき行程で逆になるので、この方法によると各層間はホスト分子の親水基と親水基、ホスト分子の疎水基と疎水基が向かい合うY型膜が形成される。それに対し、水平付着法は、担体を水面に水平に接触させて移しとる方法で、ホスト分子の疎水基が担体側に向いた単錯体分子層が担体上に形成される。この方法では、累積しても、成膜分子の向きの交代はなく全ての層において、疎水基が担体側に向いたX型膜が形成される。反対に全ての層において親水基が担体側に向いた累積膜はZ型膜と呼ばれる。

回転円筒法は、円筒型の担体を水面上を回転させて単分子層を担体表面に移しとる方法である。単分子層を担体上に移す方法は、これらに限定されるわけではなく、大面積担体を用いる時には、担体ロールから水相中に担体を押し出していく方法などもとり得る。また、前述した親水基、疎水基の担体への向きは原則であり、担体の表面処理等によって変えることもできる。

以上の成膜過程に於いて膜物質の面内方向の配向性制御は従来、主として表面圧の制御に依って成されていた訳であるが、膜物質が余程単純な構造の化合物、例えば直鎖脂肪酸等の場合を除き、高い秩序性を得ることは極めて困難であった。然るに本発明に於いては、包接錯体を膜物質に用いるので、高い秩序性を持つ膜を比較的簡単に得ることができる。即ち、水相上に包接錯体が膜状に析出した時点で、水素結合やファン・デル・ワールス力等に因ってホスト分子－ゲスト分子間、ホスト分子－ホスト分子間、ゲスト分子－ゲスト分子間の立体的配置は固定され、各ホスト分子及びゲスト分子は結晶格子的秩序性を持って配列する。又、ゲスト分子のみが機能性を持つ場合には、このゲスト分子への化学的修飾、即ち、疎水基や親水基の導入を行わないので、膜化に伴う機能の低下は生じない。

〔B〕水溶性を示すゲスト分子を水相に溶解させる。次にホスト分子を溶剤に溶解せしめてこれを水相上に展開させる。この時同時にホスト分子－ゲスト分子間で包接錯体形成が行われて膜状に析出する。ホスト分子とゲスト分子の組み合わせ及び以下の成膜操作については〔A〕に示した方法に準ずる。

〔C〕水溶性を示すゲスト分子を水相に溶解させる。次に、目的とする包接錯体のホスト分子とゲスト分子とを溶剤に溶解し、これを水相上に展開させて包接錯体を膜状に析出させる。ホスト分子とゲスト分子の組み合わせ及び以下の成膜操作については〔A〕に示した方法に準ずる。

〔D〕ホスト分子を溶剤に溶解しこれを水相中に展開させる。その後、密閉系の装置を用いて気相側、即ち装置内の空間をゲスト分子ガス雰囲気とする。この時、同時に気相側のゲスト分子を包接し、包接錯体が膜状に析出する。この方法はゲスト分子が低沸点で気化し易い性質を持つ化合物、例えばアセトン等の場合、特に有効である。ホスト分子とゲスト分子の組み合わせ及び以下の成膜操作については〔A〕に示した方法に準ずる。

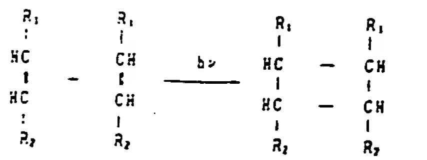
〔E〕密閉系の装置を用いて気相側、即ち装置内の空間をゲスト分子ガス雰囲気とする。次に目的とする包接錯体のホスト分子とゲスト分子とを溶剤に溶解し、これを水相上に展開させて包接錯体を膜状に析出させる。ホスト分子とゲスト分子の組み合わせ及び以下の成膜操作については、〔A〕に示した方法に準ずる。

上述の方法によって担体上に形成される単錯体分子膜及び単錯体分子層累積膜は高密度でしかも高度の秩序性を有しており、これらの膜で記録層を構成することによって、包接錯体の機能に応じて光記録、熱的記録、電気的記録あるいは磁気的記録等の可能な高密度で高解像度の記録機能を有する記録媒体を得ることができる。

作成した単錯体分子膜及び単錯体分子層累積膜を記録媒体の記録層として用いる場合以下に示す様な記録法が考えられる。

ゲスト分子の光二量化反応を用いることができる。例えばホスト分子にNo.7～15、No.22～30の何れかと、No.31-38等の光二量性二重結合を有するゲスト分子とを組み合わせるとホスト分子

対ゲスト分子の組成比（mol 比）が1：2の包接錯体が形成される。この単錯体分子膜、若しくは、単錯体分子層累積膜にあるパターンに従ってガンマ線、X線、紫外線など重合に必要なエネルギーを供給しうる光を照射すると照射部位においてⅢ式に示すようにゲスト分子間で二量化反応がおこる。



（Ⅲ）

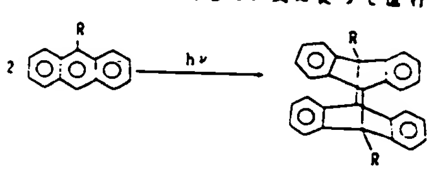
これらの反応は互いに隣接する不飽和結合の距離が4Å以下のときおこり得るものであるが、先に述べた様な方法で作成された単錯体分子膜又は、単錯体分子層累積膜では、二量化物が容易に得られるのみならず、二量化反応に伴って生成が考えられる各種の異性体若しくは構造体の唯一種しか生成されない。即ち、包接錯体層に於けるゲスト分子間の立体配列は、極めて整然としている。また、二量化した後は、暗所下でも解重合は起らず、非照射部位は単量体のままであるので、第1図に示すように、或るパターンに従った記録が成される。

記録された情報の読み取りは例えば可視光の照射によって行なう。すなわち、重合によって単量体時の共役系が崩れるので、可視光の吸収波長に変化をきたす。最大吸収波長は低波長側にシフトするので、吸収スペクトル変化を読みとることにより情報の再生が行なわれる（第2図）。

再生は、可視光による吸収スペクトル変化の読み取り以外にも、単量体時と二量化後の体積変化又は屈折率変化をシュリーレン法により読みとることも可能である。この方法は、単量体時と二量化後の体積変化又は屈折率変化の大きい構造を有する化合物の単錯体分子膜または単錯体分子層累積膜のときには特に適している。また、単錯体分子膜または単錯体分子層累積膜を基板の上に直接ではなく、基板上にSe、ZnO、CdSなどの光導電体層を形成し、その上に単錯体分子膜または単錯体分子層累積膜を形成することにより、単量体と二量体の吸光度の差を電気的に読み取ることも可能である。

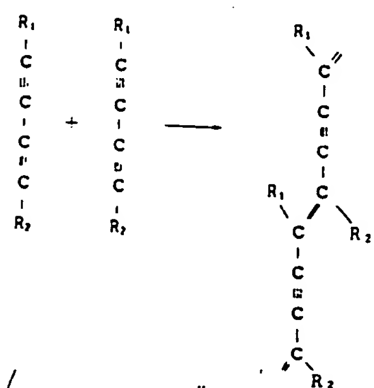
二量体はシクロブタン環に基づく、波長270nmの吸収を持つが、この波長270nmの紫外光を照射することによって二量体は元の単量体二分子に戻る。従って一度記録された情報の消去が可能となる。（第3図）

なお光二量性のゲスト分子としてアントラセン誘導体 No.39の如き化合物を用いる事もできる。この場合光二量化反応はⅣ式に従って進行する。



（Ⅳ）

又、ホスト分子として No.7 を用いた場合には、X線、ガンマ線、紫外線等の重合に必要なエネルギーを供給し得る光を照射すると、照射部位に於いてV式に示す様にホスト分子間で重合がおこり、ポリジアセチレンが形成される。



（V）

$$\left(R_1 = CH_3-(CH_2)_m-\overset{H}{\underset{OH}{C}}- \quad , \quad R_2 = HOOC-(CH_2)_n-\overset{H}{\underset{OH}{C}}- \qquad 30 \geq m+n \geq 9 \; , \; n \geq 0 \right)$$

従って、単錯体分子膜若しくは単錯体分子層累積膜に全面露光することにより、基板との付着力を飛躍的に増大せしめることが可能である。特に耐薬品（耐溶剤）性が増大する。かかる、全面露光により、ゲスト分子が光二量性を示す場合にはゲスト分子も、二量化してしまうが、これを光記録媒体として用いる際には、前述例とは逆にパ

ターンに従ってシクロブタン環の吸収波長に等しい波長の光（紫外光）を照射して解重合させることにより記録乃至表示が出来る訳である。

以上述べた記録媒体に於いて膜厚は、特に100 ～3000Åのものが好ましい。

これら成膜方法はその原理からも分る通り、非常に簡易な方法であり、上記のような優れた記録機能を有する記録媒体を低コストで提供することができる。

以上述べた、本発明における単鎖体分子膜または単鎖体分子累積膜を形成する担体は特に限定されないが、担体表面に界面活性物質が付着していると、単鎖体分子層を水面から移しとる時に、単鎖体分子膜が乱れ良好な単鎖体分子膜または単鎖体分子層累積膜ができないので担体表面が清浄なものを使用する必要がある。使用することのできる担体の例としては、ガラス、アルミニウムなどの金属、プラスチック、セラミックなどが挙げられる。

担体上の単鎖体分子膜または単鎖体分子層累積膜は、十分に強く固定されており担体からの剥離、剥落を生じることはほとんどないが、付着力を強化する目的で担体と単鎖体分子膜または単鎖体分子層累積膜の間に接着層を設けることもできる。さらに単鎖体分子層形成条件例えば水相の水素イオン濃度、イオン種、水温、担体上げ下げ速度あるいは表面圧の選択等によって付着力を強化することもできる。

単分子膜または単分子層累積膜の上に保護膜を設けることは、単分子膜または単分子層累積膜の化学的安定性を向上させるためには、好ましいことであるが、成膜分子の選択によって保護膜は設けても設けなくてもよい。

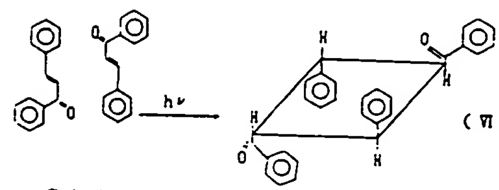
以下に本発明の実施例を示して更に具体的に説明する。No.49～ No.54の化合物は、第１表に示す。

実施例１

ゲスト分子の光二量化反応を用いた光記録媒体（１）

ホスト分子として No.49のジアセチレオンジオールと、ゲスト分子としてカルコンをモル比１：２の割合でクロロホルムに溶かした後、pH6.5 、塩化カドミウム濃度 4×10^{-4} Mの水相上に展開させた。溶媒のクロロホルムを蒸発除去し、表面圧を35dynes/cmまで高めて、包接錯体を膜状に析出させた。この後、表面圧を一定に保ちながら、表面が十分に清浄で親水性となっているガラス基板を上下速度7cm/min にて水面を横切る方向に静かに上下させ、単鎖体分子膜を基板上に移し取り、単鎖体分子膜及び３，５，９，15，19層に累積した単鎖体分子層累積膜を記録層とする光記録媒体を製造した。この累積行程に於いて基板を水相から引きあげる都度に、30分間以上放置して、基板に付着している水分を蒸発除去した。なお成膜装置としては、英国 Joyce社製のLangmuir-Trough4を使用した。

作成した光記録媒体にパターンに従って、X線照射を行い、式Ⅵに示すゲスト分子の二量化反応を行ない情報を記録した。分子オーダーの高密度記録が可能であった。



（Ⅵ）

カルコン

記録の再生はゲスト分子の二量化に伴う波長380nm～ 420nm付近の吸収変化を読み取る事により行った。次いで波長 270 nm の紫外光を１時間照射したところ、解重合がおこり、記録が消去がされた。

実施例 2～12

実施例１のカルコンの代わりにゲスト分子として No.31～ No.38の化合物を用いた場合も同様の結果を得た。（実施例 2～9）

又、ゲスト分子をカルコンとし、ホスト分子を No.50～ No.52とした場合にも、実施例１と同様、光に依る記録、再生、更には、記録の消去が

可能であった。(実施例10～12)

実施例13～24

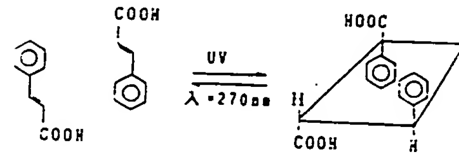
ゲスト分子の光二量化反応を用いた光記録媒体(2)

実施例1～12で述べた各光記録媒体を先ず高圧水銀灯により全面露光せしめて、全てのゲスト分子を二量化した。かかる媒体に二量化に伴って生成されたシクロブタン環の吸収極大に相当する波長270nm付近の紫外光をパターン状に照射し、ゲスト分子を解重合し情報を記録した。分子オーダーの記録が可能であった。記録の再生は、ゲスト分子の解重合に伴う波長380～420nm付近の吸収変化を読み取る事により行った。更に再び高圧水銀灯を用いて上記媒体を全面露光することにより、記録を消去、即ち、全てのゲスト分子を二量化することが可能であることを確認した。

実施例25

ゲスト分子の光二量化反応を用いた光記録媒体(3)

ホスト分子としてNo.53のジアセチレンジオール、ゲスト分子としてケイ皮酸を用いて、実施例1と同様の操作により単分子膜及び、これを3、5、9、15、19層に累積した。単分子層累積膜を記録層とする光記録媒体を製造した。次に高圧水銀灯を用いて、これらの膜を全面露光して、ゲスト分子を二量化(式Ⅶ)、ホスト分子を重合(式Ⅴ)させた後、パターンに従って、波長270nmの紫外光を照射して、ゲスト分子を解重合させて情報を記録した。分子オーダーの記録が可能であった。


(Ⅶ)

記録の再生は、二量化したゲスト分子の解重合に伴う波長380～420nm付近の吸収変化を読み取る事により行った。

更に再び高圧水銀灯を用いて上記媒体を全面露光することにより記録を消去することが可能であることを確認した。なお一度高圧水銀灯で全面露光した本記録媒体を、アルコール中に約30秒間浸漬した後、上記方法により情報の記録/再生を行ったが、特に問題点はなかった。即ち、ホスト分子を重合させる事により該記録媒体の化学的強度が大となることが確認された。

実施例26、27

ホスト分子としてNo.53のジアセチレンジオール、ゲスト分子としてアントラアルデヒドをモル比1:2の割合でクロロホルムに溶かし、実施例1と同様に操作により単分子膜及びこれを5、9、15、31、60、80層に累積した単分子層累積膜を記録層とする光記録媒体を製造した。

作成した光記録媒体にパターンに従ってX線照射を行ない、式(Ⅳ)に示すゲスト分子の二量化反応を行ない情報を記録した。分子オーダーの記録が可能であった。記録の再生はゲスト分子の二量化に伴う波長370～390nm付近の吸収変化を読み取る事により行った。次いで、波長313nmの紫外光を1時間照射したところ解重合が起こり、記録の消去が可能であることを、確かめた。

No.41のアントラセン誘導体を用いた場合にも同様の結果を得た。(実施例27)

第1表

	基本骨格	
No.49	No.10	m = 9 , n = 2
No.50	No.25	Z=COOH, n = 2
No.51	No.15	m = 9 , n = 2
No.52	No.30	Z=COOH, n = 4
No.53	No.7	m = 8 , n = 8
No.54	No.4	m = 9 , n = 2

4.図面の簡単な説明

第1図～第3図は、本発明に係る記録媒体の実施例を説明する縦断面図であり、各々、第1図は記録過程、第2図は再生過程、第3図は消去過程を示しており、第4図～第5図は本発明に係る包接錯体の水相上に於ける状態を説明する説明図である。

1…ホスト分子　　2…ゲスト分子

3…親水性部位

4…長鎖アルキル部位

5…基板

6…X線

7…二量化部位　　8…可視光

9…紫外線

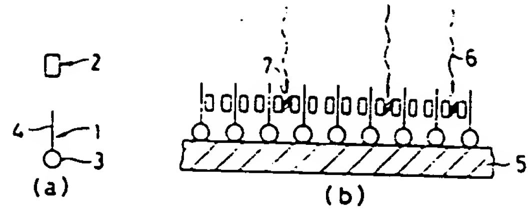
10，11…包接部位

12，13…被包接部位

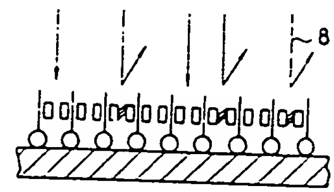
14…長鎖脂肪酸部位

15…親水性部位

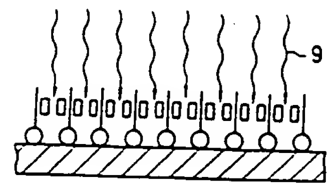
16…水相



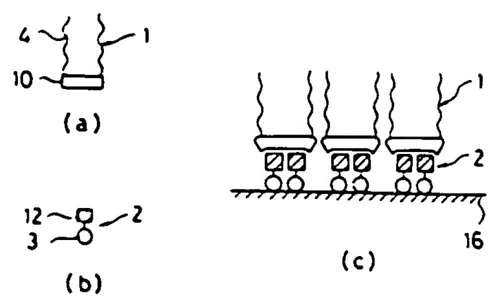
第1図



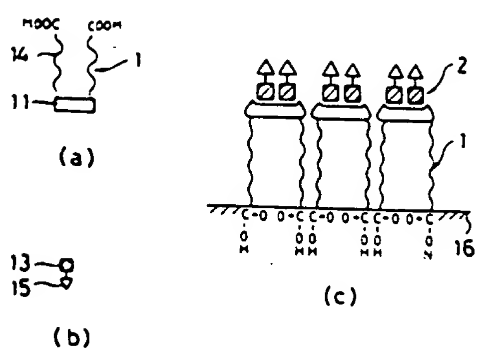
第2図



第3図



第4図



第5図